

CHELATING EQUILIBRIA OF 2-(5-BROMO-2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOL AND 4-(2-PYRIDYLAZO)RESORCINOL WITH La(III) IONS

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Received April 15th, 1987

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) with lanthanum(III) ions in 50% (v/v) aqueous ethanol or 30–50% (v/v) aqueous dimethylformamide (DMF) forms unprotonated chelates ML and ML₂ characterized by a double absorption band with maxima at 550 and 570 nm. The ML₂ species is rather unstable, hydrolyzing readily to the M(OH)L chelate, which exhibits an absorption maximum at 570 nm. The molar absorptivities of the ML, ML₂, and M(OH)L species, lying in the regions of 5.3–6.5, 7.0–7.2, and 6.5–7.2 m² mmol⁻¹, respectively, depend on the kind and fraction of the organic component in the solvent. The conditional equilibrium constants ($-\log \beta_{pqr}^*$ = 3.3–4.0, 12.2–12.5, and 7.8–8.2, respectively) decrease with increasing fraction of the organic solvent; in systems with high proportions of ethanol or DMF, the formation of higher species is greatly suppressed. 4-(2-Pyridylazo)resorcinol (PAR) with La(III) in acid aqueous solutions forms the MLH and ML species with absorption maxima at 490 and 506 nm, respectively (ϵ = 1.2 and 2.5 m² mmol⁻¹, respectively) and with conditional equilibrium constants $-\log \beta_{pqr}^*$ = -3.4 and 3.5, respectively. In alkaline solutions with excess PAR, the ML₂ species with the absorption maximum at 509 nm (ϵ = 4.6 m² mmol⁻¹) and conditional equilibrium constant $-\log \beta_{pqr}^*$ = 8.1 is formed. This chelate hydrolyses readily forming the M(OH)L species and other hydrolysis products. The ML₂ species of the two reagents, forming in ammoniacal buffer at pH 9.0–9.5 (PAR) and 8.2–8.4 (BrPADAP), can be used for a sensitive (ϵ = 3.8 and 6.1 m² mmol⁻¹, respectively) post-column derivatization of lanthanoids after their separation by IEC or HPLC or for their FIA determination.

N-Heterocyclic azo dyes are among highly sensitive organic reagents suitable for the spectrophotometric determination of ions of transition elements in trace concentrations^{1–3}. They also find wide application as metalochromic indicators for chelometric titrations^{4–6} and as derivatization agents for spectrophotometric post-column detection in HPLC or IEC (refs^{7–11}).

In this group of reagents, those of the 4-(2-pyridylazo)resorcinol (PAR) or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) type belong to the most sensitive and promising reagents for the determination of Zn(II), Cd(II), U(VI), Fe(III), and other metal ions, including lanthanoids^{12–29}. It is particularly BrPADAP that gives very sensitive and highly contrastive reactions with many metal ions^{12–27}, the selectivity of the reactions, however, is poor.

Interactions of some lanthanoids and their relatives have been studied largely in solutions with excess metal ions²³⁻²⁹ ($c_M > c_L$), where chelates with the molar ratio $M : L = 1 : 1$ are predominantly formed while the formation of higher species is suppressed. The formation of the MLH and ML species in solutions with excess Ln(III) has been proved unambiguously²⁷⁻²⁹. Considerably more important for the practice is the knowledge of interactions in solutions with excess ligand ($c_L > c_M$), which, however, are understood to a much lesser extent. Data pertaining to the occurrence of higher chelates with the molar ratio $M : L = 1 : 2$ date rather far back and have been obtained based on the determination of the stoichiometric coefficients, e.g. by the molar ratios or continuous variations methods, which occasionally fail to afford correct results. The existence of the ML_2 chelates is regarded as probable²³, or it is stated that the equilibria under these experimental conditions are very complex²³⁻²⁹.

BrPADAP, which possesses the same analytical group but where the *p*-hydroxy group is replaced by a *p*-dialkylamino group, has a considerably simpler reaction scheme of acid-base and chelating equilibria, because in the most important acidity region, pH 3–10, only the electroneutral acid-base species LH exists in the solution. Also, the presence of the *p*-dialkylamino group brings about a marked increase in the sensitivity and colour contrast of the reactions. A drawback of BrPADAP lies in the lower solubility of the reagent and its chelates in aqueous systems¹²⁻¹⁷.

In the present work, reactions of lanthanum(III) ions with PAR in aqueous solutions and with BrPADAP in 10–50% (v/v) aqueous ethanol or dimethylformamide (DMF) are studied over wide concentration and acidity regions, and the applicability of the two chemicals as derivatization reagents for post-column detection of lanthanoids after their separation by HPLC or IEC and as reagents for flow injection analysis (FIA) is assessed.

EXPERIMENTAL

Chemicals and Apparatus

Stock solutions of BrPADAP in concentrations of 0.1–1.0 mmol l⁻¹ were prepared by dissolving the solid chemical of chromatographic purity (Merck, Darmstadt, F.R.G.) in ethanol or DMF.

Stock solutions of PAR in concentrations of 0.1–1.0 mmol l⁻¹ were prepared by dissolving the recrystallized sodium salt of 89.7% purity (Lachema, Brno, Czechoslovakia) in water.

Standard solution of La(III), $c = 10$ mmol l⁻¹, was obtained by dissolving La(NO₃)₃·6 H₂O of reagent grade purity (Reakhim, Moscow, U.S.S.R.) in HNO₃ (0.1 mol l⁻¹). The concentration of La(III) was determined chelometrically using xylenol orange as the indicator. Working solutions were prepared by diluting this standard solution with HNO₃ (0.1 mol l⁻¹).

DMF was redistilled at 55–56°C/∼3 kPa. Ethanol contained 5.0% (v/v) methanol and 4.5% (v/v) water and was distilled with an addition of EDTA (1 g l⁻¹). The other chemicals used were of reagent grade or better purity. The ionic strength was kept at $I = 0.10$ with a mixture of HNO₃ and NH₃ or NaOH.

Acidity was measured with an OP 208/1 pH-meter equipped with an OP 0808P combined electrode (Radelkis, Budapest, Hungary). For simplicity, the acidities in the water-ethanol and water-DMF mixed solvents are denoted pH throughout this paper, and uncorrected values are given.

Spectrophotometric measurements were carried out on a Specord M 40 digital double beam recording spectrophotometer at an average temperature of $24 \pm 1^\circ\text{C}$ in quartz cells of 10 mm optical pathlength. The absorbances were obtained from the built-in printer as averages of ten replicate measurements with a standard deviation $s_{\text{inst}}(A) = 0.002$ absorbance units.

The equilibrium constants and molar absorptivities were calculated from sets of experimental absorbance matrices $A = f(\text{pH}, \lambda)$ or $A = f(c_L, \lambda)$ and $A = f(c_M, \lambda)$ using the program SQUAD for general regression³⁰ in the SQUAD 84 version³¹ for the EC 1 033 computer. This program seeks for $\log \beta_{\text{pqr}}^*$ and ϵ values such as give the minimal sum of residual squares $U = \sum (A_{\text{obs}} - A_{\text{calc}})^2$, where A_{obs} are the observed absorbances and A_{calc} are the calculated absorbances obtained via the $\log \beta_{\text{pqr}}^*$ and ϵ values used. The summation is performed over all wavelength values and all values of the independent variable (pH, c_L , c_M). In addition, the program SQUAD 84 enables us to calculate the rank of the absorbance matrix. Knowing the standard deviations of the experimental data $s_{\text{inst}}(A)$ and of the rank of the absorbance matrix $s_k(A)$, the number of absorbing species in the solution can be "a priori" established³², this number being identical with the rank of the absorbance matrix if $s_k(A) \approx s_{\text{inst}}(A)$.

The dissociation constants of the acid-base species of PAR and BrPADAP were also determined by numerical processing of the absorbance-pH curves for the various wavelengths using the program SIMPLEX (ref.³²) for the IQ 151 computer (ZPA, Nový Bor, Czechoslovakia), based on the simplex approach³³.

RESULTS AND DISCUSSION

Reactions of La(III) with BrPADAP

Over the wide region of pH 3.5–10, BrPADAP occurs as the yellow electroneutral acid-base species LH. At pH ≈ 1 , the protonated species LH_2^+ exists whereas at pH > 10 , the proton of the *o*-hydroxy group dissociates to give rise to the anionic species L^- . Optical characteristics of the various acid-base species and the corresponding acid-base properties are given in Table I.

The molar absorptivities of the acid-base species were calculated by the SQUAD 84 program for the wavelength region of 410–600 nm at a step of 10 nm. Since the program does not enable the position of the absorption maximum to be determined accurately by interpolation, the SPECTRUM 1 program³² was employed for an accurate determination of the positions of the absorption maxima and isobestic points; this program approximates the $\epsilon = f(\lambda)$ curve by a Chebysheff polynomial whose degree is either entered directly from the computer keyboard or is determined by the Fischer criterion.

Table I demonstrates that the calculated λ_{max} and ϵ_{max} values for the acid-base species LH and LH_2^+ agree well with those determined from the spectral scan or obtained from the printer of the instrument in the automatic mode. The most important data for BrPADAP are obtained by the SPECTRUM 1 program for the

species L^- , because experimental conditions under which this species is present in the solution solely ($\text{pH} = \text{p}K_{a1} + 2 \gtrsim 13$) are difficult to adjust without substantial variation of ionic strength; the absorption spectra are invariably distorted in this pH range. The obtained optical characteristics of all the BrPADAP acid-base species agree well with published data¹²⁻¹⁷.

The dissociation constants for the LH_2^+/LH and LH/L^- acid-base transitions were obtained by the SIMPLEX program at $\lambda = 445, 485, \text{ and } 512 \text{ nm}$, $c_L = 20 \mu\text{mol l}^{-1}$, and $\text{pH } 1-12$. These $\text{p}K_{a1} \pm s(\text{p}K_{a1})$ values, viz. $\text{p}K_{a1} = 2.73 \pm 0.03$, $\text{p}K_{a2} = 10.89 \pm 0.05$, are in a very good agreement with those obtained by the SQUAD 84 program in the above experimental conditions at $\lambda = 410-600 \text{ nm}$ with a step of 10 nm , viz. $\text{p}K_{a1} = 2.77 \pm 0.01$, $\text{p}K_{a2} = 10.93 \pm 0.01$, and also with published data¹²⁻¹⁵.

The standard deviations $s(A)$ for the regions of $\text{pH } 1-7$ and $\text{pH } 8-13$ corresponding to the two acid-base transitions, viz. $s(A) = 5.38 \cdot 10^{-3}$ and $8.65 \cdot 10^{-3}$ absorbance units, respectively, obtained for 23 and 18 experimental pH values, respectively, and 20 discrete wavelengths, are consistent with the values of $s_{\text{inst}}(A) \leq 0.01$ absorbance units.

TABLE I

Optical characteristics of the acid-base species of PAR in aqueous solution ($c = 40 \mu\text{mol l}^{-1}$) and BrPADAP in 10% (v/v) ethanol ($c = 20 \mu\text{mol l}^{-1}$); $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$)

Species	λ_{max}^a nm		ϵ_{max}^a $\text{m}^2 \text{mmol}^{-1}$		$\lambda_{\text{ip}}^{a,b}$ nm		ϵ_{ip}^b $\text{m}^2 \text{mmol}^{-1}$
PAR							
LH_3^+	395	395	1.6	1.63 ± 0.01	390	391	1.63 ± 0.02
LH_2	383	385	1.7	1.65 ± 0.01	379	379 ^c	1.63 ± 0.02^c
LH^-	413	411	2.7	2.67 ± 0.02	448	447	1.33 ± 0.03
L^{2-}	490	488	2.0	2.16 ± 0.01	—	—	—
BrPADAP							
LH_2^+	468	466	4.5	4.53 ± 0.01	456	455	4.23 ± 0.04
LH	445	444	4.4	4.57 ± 0.02	476	477	3.01 ± 0.04
L^-	515	513	4.7	4.54 ± 0.03	—	—	—

^a Experimental data obtained from the graphical record of the absorption spectra or from spectrophotometer printout (column 1) and data calculated by SPECTRUM 1 program³² (column 2);

^b parameters of isosbestic points for the acid-base transitions LH_3^+/LH_2 , LH_2/LH^- , and LH^-/L^{2-} for PAR and LH_2^+/LH and LH/L^- for BrPADAP; ^c values of 463 nm and $0.52 \pm 0.03 \text{ m}^2 \text{mmol}^{-1}$ for the second isosbestic point.

For BrPADAP, mixed aqueous solvents containing 10–50% (v/v) ethanol or DMF were employed with regard to the low solubility of this reagent and its metal ion chelates^{12–27} in purely aqueous solutions. Addition of nonionic or ionic surfactants such as BRIJ 35 or TRITON X-100 (0.01–1.0%), and SDS (0.1–1 mmol l⁻¹) did not bring about appreciable changes in the optical characteristics of the chelates.

Interaction of BrPADAP ($c_L = 20 \mu\text{mol l}^{-1}$) with La(III) ions ($c_M = 2 \text{ mmol l}^{-1}$) in weakly basic to weakly acid solutions (pH < 8) manifests itself in the absorption spectrum by the appearance of a double absorption band with maxima at 540 and 560 nm (Fig. 1). The absorbance–pH curves of solutions with a 50–100-fold excess of La(III) ions exhibit a broad plateau at pH 7.6–8.4. If the concentration excess is increased, the ascending parts and plateaus of the absorbance–pH curves shift to more acid values (Fig. 2). The repeatability of measurement at pH > 7.3 is considerably poorer ($s_{\text{inst}}(A) \approx 0.02\text{--}0.03$ absorbance units) due to hydrolysis of La(III) and its chelates.

Experiments in solutions with excess BrPADAP are hampered by the low solubility of this reagent (at $c_L > 0.2 \text{ mmol l}^{-1}$) also in 30% (v/v) DMF or 50% (v/v) ethanol. The absorbance–pH curves are distorted considerably, exhibiting a plateau at pH 7.5–8.0. Quantitative chelation is not attained even at a 50-fold excess of BrPADAP ($c_L = 0.2 \text{ mmol l}^{-1}$).

In 30% (v/v) DMF, the absorbance–pH curves are also shifted to more acid values and at a 20–50-fold excess of BrPADAP, plateaus of 0.2–0.3 pH units appear on the curves over the pH 8.0–8.2 range. The absorbances in the plateaus nearly

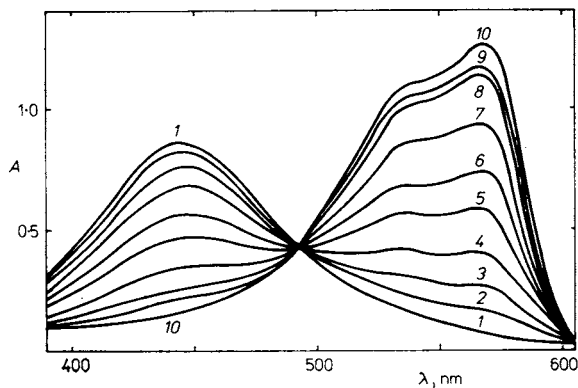
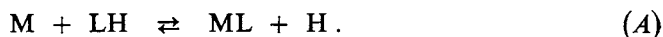


FIG. 1

Absorption spectra of La(III) with BrPADAP in 30% (v/v) DMF; $c_L = 20 \mu\text{mol l}^{-1}$, $c_M = 2.000 \mu\text{mol l}^{-1}$, $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$). pH: 1 4.34, 2 5.26, 3 5.67, 4 5.89, 5 6.32, 6 6.65, 7 7.01, 8 7.30, 9 7.45, 10 8.13

correspond to the quantitative reaction yield (Fig. 2). At $\text{pH} > 8.2$, the absorbance is highly time-dependent and the repeatability of measurements is very poor ($s_{\text{inst}}(A) \leq 0.02$ absorbance units) due to the occurrence of hydrolysis equilibria of La(III) and its chelates; this repeatability is about one-and-a-half orders of magnitude poorer than that for measurements at lower pH values. These experimental data were therefore omitted from the calculations by the two methods.

Graphical interpretation of the absorbance-pH curves of solutions with a 50 to 100-fold excess of La(III) gives unambiguous evidence of the formation of a simple chelate with the molar ratio $M : L = 1 : 1$ in the sense of the equilibrium (charges are omitted for simplicity)



The conditional equilibrium constants for this equilibrium agree well with those obtained numerically by the SQUAD 84 program (Table II).

The same result can be obtained by the graphical methods for the equilibrium³⁴⁻³⁷ between La(III) and BrPADAP giving rise to the $M(\text{OH})LH$ species in the sense of the equilibrium

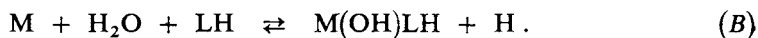


Table II gives the results of numerical processing by the SQUAD 84 program of the absorbance-pH curves for solutions with different La(III)-to-BrPADAP ratios in terms of the equilibrium

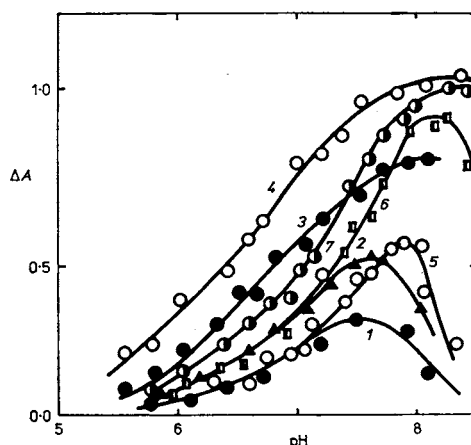
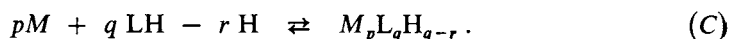


FIG. 2

Absorbance-pH curves for solutions of La(III) with BrPADAP in 30% (v/v) DMF, $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$), $\lambda = 550$ nm, $l = 10$ mm; c_L, c_M ($\mu\text{mol l}^{-1}$): 1 20, 1 000; 2 20, 200; 3 20, 1 000; 4 20, 2 000; 5 40, 20; 6 200, 20; 7 400, 20

Data obtained for the wavelength regions of 380–600 nm (excess La(III)) and 540–600 nm (excess BrPADAP) with a step of 10 nm were employed. The narrow region in the latter case was used with regard to the high absorbance values at wavelengths in the range of the absorption maximum of the electroneutral BrPADAP species. The acidity ranges were pH 5–7 (excess La(III)) and pH 4–7.2 (excess BrPADAP), whereby the effect of the poor repeatability in the alkaline region was eliminated.

TABLE II

Conditional stability constants of La(III)–BrPADAP chelates in water–ethanol and water–DMF systems; $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$), matrix rank $N = 3$

Solvent	$-\log \beta_{111}^*$	$-\log \beta_{112}^*$	$-\log \beta_{123}^*$	$s(A)$
10% ethanol	3.60 ± 0.003^a	12.70 ± 0.20^a	—	4.6
	$3.69 \pm 0.02^{a,b}$	—	—	—
	3.73 ± 0.05^c	—	—	11.3
30% ethanol	3.85 ± 0.02^a	12.27 ± 0.06^a	—	8.1
	$3.82 \pm 0.05^{a,b}$	—	—	—
	3.81 ± 0.02^d	—	—	21.0
50% ethanol	4.03 ± 0.01^a	—	—	9.9
	—	—	7.86 ± 0.03^e	13.2
10% DMF	3.30 ± 0.002^a	12.23 ± 0.02^a	—	2.5
	$3.30 \pm 0.02^{a,b}$	—	—	—
30% DMF	3.76 ± 0.002^a	12.23 ± 0.12^a	—	3.3
	$3.70 \pm 0.03^{a,b}$	—	—	—
	3.75 ± 0.03^f	—	8.20 ± 0.13^f	11.2
	3.66 ± 0.02^g	—	—	17.2
	3.53 ± 0.02^h	—	—	25.8
50% DMF	3.83 ± 0.002^a	12.47 ± 0.05^a	—	2.7
	$3.80 \pm 0.03^{a,b}$	—	—	—
	3.81 ± 0.05^i	12.40 ± 0.13^i	—	10.3
	3.66 ± 0.02^j	—	—	26.3

^a $c_L = 20 \mu\text{mol l}^{-1}$, $c_M = 2\,000 \mu\text{mol l}^{-1}$; ^b graphical method for $\lambda = 550 \text{ nm}$; ^c simultaneous processing of curves for $c_L = 20 \mu\text{mol l}^{-1}$, $c_M = 200$ and $2\,000 \mu\text{mol l}^{-1}$; ^d simultaneous processing of curves for $c_L = 20 \mu\text{mol l}^{-1}$, $c_M = 200$ and $1\,000 \mu\text{mol l}^{-1}$; ^e $c_L = 400 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$; $\log \beta_{111}^* = 4.03$ and molar absorptivity of LaL chelate used as fixed values; ^f $c_L = 400 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$; ^g $c_L = 200 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$; ^h simultaneous processing of curves for $c_M = 20 \mu\text{mol l}^{-1}$, $c_M/c_L = 50$ and 100 ; ⁱ $c_L = 1\,000 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$; ^j $c_L = 800 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$, $\log \beta_{112}^* = -12.40$ used as a fixed value.

The results document that the ML species predominates in the two mixed solvents. Both its stability and its absorptivity in the absorption maximum (Table III) are negatively affected by increasing fraction of the organic component of the solvent system. In solutions with excess BrPADAP, the ML₂ and M(OH)L species are also formed; their stability and absorption intensity are also affected negatively by increasing fraction of the organic cosolvent.

The stability of the ML₂ chelate is higher in the ethanolic system than in the DMF system under otherwise identical conditions and it is so low in solvents with high fractions of the organic component that in 30% (v/v) DMF, this chelate is only formed at a 40-fold excess of BrPADAP and it is virtually absent from solutions in 50% (v/v) ethanol even at a 50-fold excess of reagent.

In such extreme cases, the calculations by the SQUAD 84 program converge with a sufficient agreement of the parameters (Tables II and III) only if the formation of the ML₂ species or a mixture of the ML and ML₂ species is considered. For a mixture of the ML, M(OH)L, and ML₂ species in the two solvent systems, for the

TABLE III
Molar absorptivities of La(III)-BrPADAP chelates $I = 0.10$ (HNO₃ + NH₃)

Solvent	λ_{\max} nm	$\epsilon_{\max}, \text{m}^2 \text{mmol}^{-1}$		
		ML	M(OH)L	ML ₂
10% ethanol	570	5.99 ± 0.02^a	—	—
	570	5.65 ± 0.09^c	—	—
30% ethanol	560	5.78 ± 0.04^c	—	—
	560	5.32 ± 0.12^d	—	—
	570	—	6.88 ± 0.08^a	—
50% ethanol	560	5.36 ± 0.05^a	—	—
	570	—	—	7.06 ± 0.09^e
10% DMF	570	6.52 ± 0.01^a	7.19 ± 0.07^a	—
30% DMF	570	6.31 ± 0.02^a	7.08 ± 0.06^a	—
	570	5.93 ± 0.06^f	—	6.99 ± 0.08^f
	570	6.45 ± 0.05^g	—	—
	570	6.06 ± 0.08^h	—	—
50% DMF	570	5.59 ± 0.01^a	6.49 ± 0.06^a	—
	570	—	7.37 ± 0.10^i	—
	560	5.48 ± 0.17^i	—	—
	560	5.31 ± 0.09^j	7.15 ± 0.14^j	—

^{a-j} Same as in Table II.

ML₂ species solely in the DMF system, and for a mixture of the ML and ML₂ species in the ethanolic system, the calculations do not converge with a sufficient agreement of the parameters even after 20 computation cycles ($s(A) > 0.03$ absorbance units).

Processes playing the major part in the basic region at $\text{pH} > \text{pH}_{\text{opt}}$ make the repeatability of measurement considerably poorer, and require a detailed kinetic study. One of the possible causes of the slow establishment of the absorbances may be the replacement of one molecule of BrPADAP in the ML₂ species by a hydroxyl group giving rise to M(OH)L or some related species. The regions of existence of the two species are nearly identical, and the equilibrium concentration ratio depends on the experimental conditions (Fig. 3) and on time.

Reactions of La(III) with PAR

In dependence on acidity over the region of pH 1–14, PAR exists in four acid-base forms, viz. LH₃⁺, LH₂, LH⁻, and L²⁻. The three acid-base transitions are characterized by the dissociation constants pK_{a1}, pK_{a2}, and pK_{a3} corresponding to the dissociation of protons from the heterocyclic nitrogen, the *p*-hydroxy group and the *o*-hydroxy group, respectively^{19–29}.

The optical characteristics of the acid-base species of PAR are given in Table I. The dissociation constants at $c_L = 40 \mu\text{mol l}^{-1}$ were calculated by the SIMPLEX program for wavelengths of 410–450 nm at a step of 10 nm; the values obtained, viz. pK_{a1} = 2.95 ± 0.05, pK_{a2} = 5.26 ± 0.05, and pK_{a3} = 11.56 ± 0.01, agree

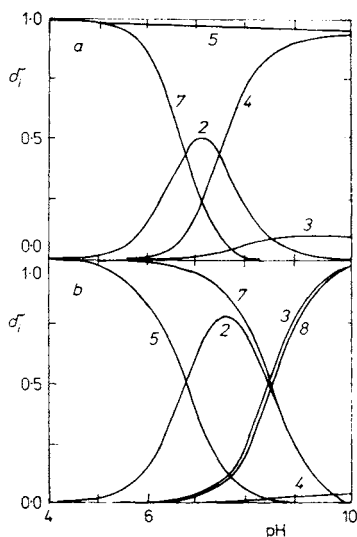


FIG. 3
Distribution diagrams of the La(III)–BrPADAP system in 50% (v/v) DMF, $I = 0.10$ (HNO₃ + NH₃); *a* $c_L = 1\,000 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$; *b* $c_L = 20 \mu\text{mol l}^{-1}$, $c_M = 1\,000 \mu\text{mol l}^{-1}$. Species: 1 MLH, 2 ML, 3 M(OH)L, 4 ML₂, 5 LH, 6 LH₂, 7 M, 8 M(OH). δ_i relates to the lower of the c_L , c_M concentrations

well with published data¹⁸⁻²⁰ as well as with data obtained by numerical processing of the absorbance-pH curves by the SQUAD 84 program³¹ at $\lambda = 360-540$ nm with a step of 10 nm over the acidity regions of pH 1-8 and pH 9-13, viz. $pK_{a1} = 3.03 \pm 0.02$, $pK_{a2} = 5.35 \pm 0.01$, and $pK_{a3} = 11.53 \pm 0.06$. The repeatabilities are $s(A) = 3.69 \cdot 10^{-3}$ and $7.98 \cdot 10^{-3}$ absorbance units for the two acidity regions, respectively, the corresponding $s_{inst}(A)$ values are 0.003 and 0.006 absorbance units, respectively.

The chelating equilibria of PAR with La(III) in solutions with excess metal ions start to be significant at $pH \approx 5$. They manifest themselves in the absorption spectra by a characteristic band with a maximum at 503 nm (Fig. 4). In solutions with excess PAR, the chelation only results in a slight distortion of the long-wavelength side of the band of the LH^- species of PAR. The chelation is rapid enough and the spectral changes appear immediately after mixing.

The characteristic shift of the absorption band is indicative of an interaction of the *o*-hydroxy group of the resorcinol and proton dissociation from this group during the chelation. It can be assumed that various PAR species with protonated or deprotonated *p*-hydroxy groups may be present in the solution because the chelating equilibria occur in a near vicinity to the LH_2/LH^- acid-base transition region. In accordance with published data, the presence of the simple ML and MLH species solely can be assumed in solutions with excess La(III). In solutions with excess PAR, a mixture of chelates with different degrees of protonation and with the molar ratios 1 : 1 or 1 : 2, together with ternary chelates of $M_mL_nX_o$ type where X can be some simple ion such as OH^- , F^- , SCN^- , etc., can be assumed to

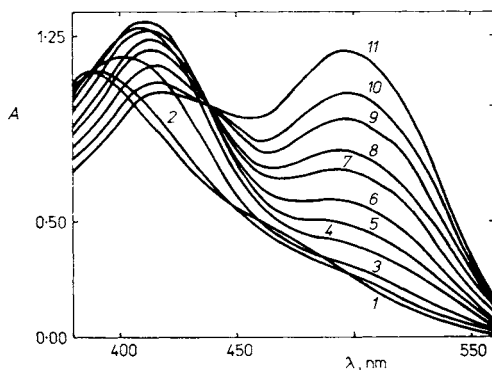


FIG. 4

Absorption spectra of La(III) with PAR in aqueous solutions, $c_L = 17.9 \mu\text{mol l}^{-1}$, $c_M = 200 \mu\text{mol l}^{-1}$, $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$), $l = 40$ mm. pH: 1 3.77, 2 4.56, 3 5.11, 4 5.63, 5 6.00, 6 6.23, 7 6.38, 8 6.50, 9 6.83, 10 7.01, 11 7.25

be present, similarly as with some other metal ions¹⁻³. The proportions of the chelates will depend on acidity, concentrations, and nature of ion X.

The absorbance-pH curves for solutions with excess La(III) ($c_L = 40 \mu\text{mol l}^{-1}$, $c_M = 200 \mu\text{mol l}^{-1}$) exhibit no marked plateau and their absorbance maximum lies at $\text{pH} \approx 7.5$. (Fig. 5). At high concentrations of La(III) ions ($c_M > 200 \mu\text{mol l}^{-1}$), hydrolysis of La(III) takes place, where upon the equilibrium establishes slowly and a precipitate separates.

A tentative analysis of the experimental data for solutions with excess La(III) and for $\lambda = 520 \text{ nm}$ by the graphical method³⁴ bears out the occurrence of a mixture of the protonated and unprotonated chelates with the molar ratio $M : L = 1 : 1$ over the entire region of La(III) concentrations and $\text{pH} 4-8$. At lower pH values and higher concentrations of La(III), the MLH species ($\epsilon = 1.23 \text{ m}^2 \text{ mmol}^{-1}$) prevails, whereas at higher pH values, the ML species ($\epsilon_{500} = 2.24 \text{ m}^2 \text{ mmol}^{-1}$) is predominantly formed.

The chelation can be represented by the equation



(charges are omitted for simplicity). The stoichiometric coefficients i , x , y , w can be only determined if the chelating equilibria and the probability of interactions of the various acid-base species and La(III) hydrolysis products are known. Independent determination of the coefficients x and y in the $\text{M}_p(\text{OH})_x \text{L}_q \text{H}_y$ species is practically impossible³⁵⁻³⁸; one of them can be determined if an a priori value of the other is inserted. Since hydrolysis of La(III) in dilute solutions takes place in a more basic region than its interaction with PAR, a mutual reaction of PAR with

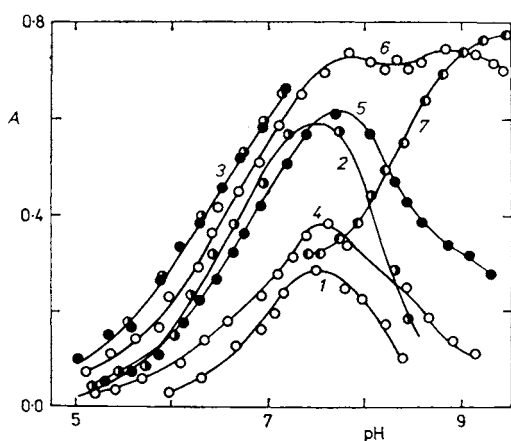


FIG. 5
Absorbance-pH curves of the La(III)-PAR system in aqueous solutions, $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$), $\lambda = 520 \text{ nm}$, $l = 10 \text{ mm}$; $c_L, c_M (\mu\text{mol l}^{-1})$: 1 35.7, 40; 2 35.7, 200; 3 35.7, 2 000; 4 107.2, 40; 5 178.6, 40; 6 354.2, 40; 7 200, 20

the simple unhydrolyzed La(III) ion can be assumed to proceed over the entire region of the experimental conditions used. This also implies that the occurrence of the ML and MLH species is considerably more probable than the occurrence of the M(OH)LH and M(OH)LH₂ species.

Thus, the most likely scheme of chelation in solutions with excess La(III) is



Data processing by the SQUAD 84 program was applied to the wavelength region of 390–560 nm at step of 10 nm and pH 4.0–8.0. Several chelation models according to Eq. (C) were treated; the concentration ratios considered are given in Table IV. The best results were obtained assuming a simultaneous occurrence of the MLH and ML chelates and using fixed values for the dissociation constants pK_{a1} and pK_{a2} and absorptivities of the LH⁻ and LH₂ acid-base species of PAR. When the formation of the ML chelate is considered under otherwise identical assumptions,

TABLE IV

Equilibrium constants $\log(\beta_{pqr}^* + s\beta_{pqr}^*)$ for the reaction $pM + qLH - rH \rightleftharpoons M_pL_rH_{q-r}$ and molar absorptivities of the MLH, ML, and ML₂ species for the La(III)-PAR system in aqueous solutions, $I = 0.10$ (HNO₃ + NH₃). Absorbance matrix rank $N = 3$

c_L $\mu\text{mol l}^{-1}$	c_M $\mu\text{mol l}^{-1}$	Chelate	$\log \beta_{pqr}^*$	$s(A)$	λ_{max} nm	ϵ_{max} $\text{m}^2 \text{mmol}^{-1}$
35.72 ^a	4 000	MLH	3.25 ± 0.01	0.005	487	0.99 ± 0.03
		ML	-3.61 ± 0.02	—	506	2.74 ± 0.02
17.86 ^a	200	MLH	3.54 ± 0.04	0.006 ^b	490	1.20 ± 0.05
		ML	-3.44 ± 0.02	—	508	2.36 ± 0.03
178.6	20	MLH ^{c,d}	—	0.011 ^e	493	1.34 ± 0.07
		ML	-3.40 ± 0.05	—	505	2.28 ± 0.05
200.0 ^f	20	ML ₂	-8.06 ± 0.12	0.034 ^g	509	4.59 ± 0.05

^a Calculated with fixed values of pK_{a1} and pK_{a2} of PAR and of molar absorptivities of its LH⁻ and LH₂ species, $l = 40$ mm; ^b model of the MLH chelate formation does not converge, model of the ML chelate formation converges with $s(A) = 0.11$, $\log \beta_{111}^* = -2.93 \pm 0.02$; ^c gradual pH adjustment by titration (pH 3.0–6.2), calculation with fixed pK_{a1} and pK_{a2} values of PAR and molar absorptivity of its LH₃⁺ species, $l = 20$ mm; ^d calculated with a fixed value of the equilibrium constant of the reaction $M + LH \rightleftharpoons ML + H$, $\log \beta_{111}^* = 3.40$; ^e models for the ML₂ or ML(OH)L chelate formation in addition to the ML and MLH chelate formation do not converge; ^f instantaneous change in acidity (pH 7.5–10.0), measurement 2–3 min after mixing, $l = 10$ mm, calculation with a fixed value of molar absorptivity of the LH⁻ species of PAR, presence of the LH₂ and LH₃⁺ species disregarded; ^g absorbance matrix rank $N = 2$.

the calculation converges with $s(A) = 0.011$ absorbance units and $\log \beta_{111}^* = -2.93 \pm 0.02$. If the formation of the MLH chelate alone or of mixtures of the MLH, ML, and ML_2 or ML and $M(OH)L$ or ML and M_2L or ML_2 or $M(OH)L$, ML, and MLH chelates is regarded, the calculations do not converge even after 20 cycles. The results of the treatment are summarized in Table IV. The hydrolysis constant of the monomeric $La(OH)$ species³⁸ was used for La(III), and fixed values of pK_{a1} and pK_{a2} and absorptivities of the LH^- and LH_2 species were entered (see Table I and the text).

The results of the numerical processing also give evidence of the occurrence of a mixture of the MLH and ML species. The absorption band of the latter species exhibits a bathochromic shift of approximately 10 nm with respect to that of the former. This spectral shift, associated with the dissociation of the *p*-hydroxy group of the MLH species, correlates with that associated with the dissociation of the electroneutral form of PAR, the same proton being split off during the two deprotonation processes.

‡ The most probable reaction scheme and the best suiting $\log \beta_{110}^*$ and $\log \beta_{111}^*$ values, giving the lowest sum of squares of $(A_{obs} - A_{calc})$ residuals and the lowest standard deviation of absorbances, pertain to the occurrence of the MLH and ML chelates.

The values of 3.08 and -3.35 determined at a tenfold excess of La(III) by the graphical methods³⁴⁻³⁷ for a wavelength of 520 nm agree well with those found by the SQUAD 84 program for a wider spectral region, and also with published data.

It is clear that the conditional dissociation constant of the MLH chelate, as an index of the acid dissociation of the *p*-hydroxy group, is equal to the difference $\log \beta_{110}^* - \log \beta_{111}^*$, viz. 6.49. This value is consistent with published data^{18-20, 23-29}. The value of the conditional equilibrium constant of the MLH chelate indicates a low stability of chelates of PAR with La(III), because for compounds of this kind, the dissociation constant of the MLH/ML transition generally decreases considerably with respect to that of the LH_2/LH^- transition as the stability of the chelate increases (for the highly stable copper chelate this change encompasses two orders of magnitude³⁹).

The absorbance-pH curves for solutions with excess PAR ($c_L = 400 \mu\text{mol l}^{-1}$, $c_M = 40 \mu\text{mol l}^{-1}$) which were obtained by gradual, slow pH adjustment by titration with NaOH from $\text{pH} \approx 3$ to $\text{pH} \approx 10$ at a step of approximately 0.2–0.3 pH units exhibit two plateaus at $\text{pH} 7.7-7.8$ and $\text{pH} \approx 9$. At lower concentrations of PAR, the second plateau transforms into an inexpressive maximum. At $c_L > 500 \mu\text{mol l}^{-1}$ a coloured precipitate separates and adsorbs strongly on the walls of the vessels and cells and on the surface of the electrodes.

The absorbance-pH curves for $c_L = 200 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$ obtained by the classical procedure in volumetric flasks with rapid pH adjustment display

a broad plateau at pH 9–10 (Fig. 5). The absorptivity at 490–500 nm is about three times higher than that calculated from the absorbance–pH curves obtained by the gradual pH adjustment, and about twice as high as the values determined from the curves for solutions with excess La(III).

The graphical interpretation of the absorbance–pH curves points to the formation of higher chelates with the molar ratio $M : L = 1 : 2$. The absorbance, however, is highly time-dependent: in the first 10 min after mixing it decreases about 5% at pH 8–8.5 and about 20% at pH 9–9.5. In 3–4 hours, the absorbance approaches that obtained on the gradual pH adjustment. In contrast to the BrPADAP–La(III) system, where a rapid absorbance change occurs even at pH 8–8.5 and at pH 9–9.5 the colour is only stable for several seconds, with PAR the measurements are reasonably reproducible over a period of 5 min.

These phenomena can be so explained that on a rapid alkalization, the higher ML_2 chelate is first formed, and this species hydrolyzes to give various hydrolysis products. A slow pH adjustment facilitates the hydrolysis process and, on the other hand, is unfavourable for the formation of the ML_2 species.

Numerical interpretation of the absorbance–pH curves by the SQUAD 84 program for $c_L = 200$ or $400 \mu\text{mol l}^{-1}$, $c_M = 20 \mu\text{mol l}^{-1}$ points to a preferential formation of a mixture of the MLH and ML chelates at pH 3.0–6.2, the spectral characteristics and equilibrium constants being in a good agreement with those obtained for solutions with excess La(III). The slightly higher $s(A)$ values are due to the possibility of formation of higher chelates ($M : L = 1 : 2$) being disregarded. The data for pH 6.2–9.5 give evidence of the occurrence of the ML_2 and/or $M(OH)L$ species. If the formation of the ML and MLH species in addition or solely was considered, the calculation did not converge or converged to unreasonable values of the equilibrium constants or absorptivities. For instance, the calculated absorptivity of the ML_2 chelate was approximately two times lower than that of the ML chelate.

The above facts indicate that for an adequate description of the chelating equilibria of PAR with La(III) in alkaline solutions, formation of polydentate products of hydrolysis of La(III) and their slow interaction with the ligands have to be taken into account. The reactions are complex and they are not quite clear. In the starting stage, anyway, the ML_2 chelate is formed, as indicated by the results given in Table IV, but it transforms slowly into $M(OH)L$ or other hydrolysis products.

Systems of La(III) with PAR and with BrPADAP have much in common. The chelating equilibria occur in weakly acid (pH > 4) to basic solutions. The interaction leads to the formation of chelates of two types, with molar ratios $M : L = 1 : 1$ and $1 : 2$, lanthanum(III) being bonded via the *o*-hydroxy group, azo group and heterocyclic nitrogen atom.

The distribution diagrams of the chelates of La(III) with PAR at a tenfold excess of either La(III) or PAR (Fig. 6) demonstrate that in weakly acid solutions, the

protonated MLH chelate is formed in fractions about 35%, highest at $\text{pH} \approx 6.1$. The ML species is formed at $\text{pH} > 5$ and the maximum fractions, about 85 and 50%, respectively, occur at $\text{pH} \approx 8.8$ and 7.6, respectively. In strongly basic solutions with excess PAR, the ML_2 chelate is formed nearly quantitatively, the optimum lying at $\text{pH} \geq 9.5$.

TABLE V

Basic characteristics of La(III)-PAR chelates in aqueous solution and La(III)-BrPADAP chelates in 30% (v/v) DMF

Quantity	PAR	BrPADAP
$c_L, \mu\text{mol l}^{-1}$	200	400
$\lambda_{\text{opt}}, \text{nm}$	520	568
$\epsilon_{\text{max}}^a, \text{m}^2 \text{mmol}^{-1}$	3.84 ± 0.06	6.10 ± 0.03
pH_{opt}	9.0-9.5	8.0-8.2
$\Delta\lambda, \text{nm}$	80	115
$c_M^b, \text{nmol l}^{-1}$	260	160

^a Conditional values calculated from calibration curves for $c_M = 0-10 \mu\text{mol l}^{-1}$, number of points $n = 6$; ^b detection limit for $A = 0.01$.

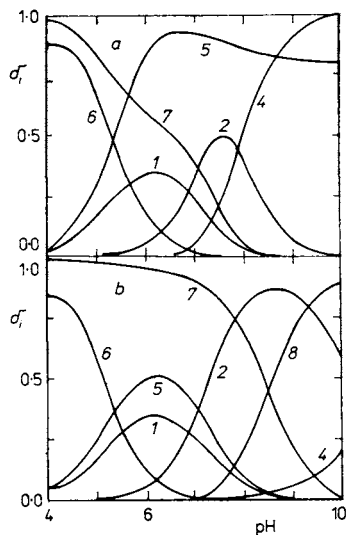


FIG. 6

Distribution diagrams of the La(III)-PAR system in aqueous solutions, $I = 0.10$ ($\text{HNO}_3 + \text{NH}_3$); **a** $c_L = 400 \mu\text{mol l}^{-1}$, $c_M = 40 \mu\text{mol l}^{-1}$; **b** $c_L = 40 \mu\text{mol l}^{-1}$, $c_M = 400 \mu\text{mol l}^{-1}$ (other conditions see Fig. 3)

The presence of the phenolic group in the *para* position with respect to the azo group thus leads to the formation of protonated chelates with PAR, which is impossible with BrPADAP where only the ML, ML₂, and M(OH)L chelate species are formed, as is clear from the distribution diagrams in Fig. 3. The ML chelate is present predominantly in weakly acid to weakly basic solutions, with the optimum of formation (50–75%) at pH 7–8. The formation of the higher chelate, ML₂, is suppressed particularly in solutions with excess La(III), and even in solutions with excess BrPADAP its fraction never exceeds 95%.

The equilibrium formation constants of the La(III) chelates with PAR and with BrPADAP are close to one another. Appreciable differences between the two reagents are in the higher colour contrast and sensitivity of the reaction of La(III) with BrPADAP on the one hand and in the higher time stability of solutions in the basic region with PAR on the other hand.

The basic optical characteristics of La(III) chelates with the two reagents are summarized in Table V. The sensitivity of the reactions is comparable to that with Arsenazo III but the time colour stability of the ML₂ chelates is a hindrance to their wide application to chemical photometric determinations. They can be used, however, for FIA measurements⁴⁰ or for the post-column derivatization⁴¹ of rare earth ions after their separation by HPLC or IEC because the time between the mixing and detection is very short (about 10–20 s) and hydrolysis processes are suppressed.

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Translated by P. Adámek.